

CORROSION BEHAVIOR OF REINFORCING STEEL IN CEMENT PARTIALLY REPLACED WITH METAKAOLIN IN 3.5% NACL AND 5% MGSO4 SOLUTIONS

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ABSTRACT

The effect of different percentages of metakaolin cement replacement on the corrosion behavior of embedded reinforcing steel bars was studied in the presence of 3.5% NaCl and 5% MgSO₄ solutions. A poor Greek kaolin with a low kaolinite content was thermally treated and the produced Metakaolin (MK) was ground to the appropriate fineness. Different electrochemical techniques namely; open circuit potential, linear polarization and electrochemical impedance spectroscopy measurements were used to investigate the corrosion behavior of the embedded reinforcing steel bars. It is found that the use of Metakaolin as a cement replacement, 20% w/w, improves the corrosion behavior of reinforcing steel in cement in 3.5 % NaCl solution. While in 5% MgSO₄ solution, the 5 % MK replacement is the ratio to reduce corrosion rate.

KEYWORDS: Corrosion Behavior, Reinforcement, Metakaolin, Electrochemical Techniques

INTRODUCTION

The durability of reinforced concrete depends on the surrounding environmental and exposure conditions. The alkaline phase from hydrated cement has a protective effect for the embedded reinforcing steel bars. Reinforcement corrosion is one of the major causes of degradation in concrete structure [1]. MK is unique in that it is not the by-product of an industrial process nor it is entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications [2]. Metakaolin, produced by controlled thermal treatment of kaolin, can also be used as a concrete constituent, since it has pozzolanic properties [3].

The studies, regarding the improvement of the mechanical, shrinkage, and some durability properties of the concrete by MK have been carried out [4–6]. Batis et al. [3] reported that the use of Metakaolin, either as a sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improved the corrosion behavior of mortar specimens.

The cement which is alkaline (pH 13.5) oxidizes embedded steel bars, forming a chemically and electrically inactive layer (passive film) of ferric oxide [7]. Corrosion of the reinforcing steel bars is initiated to form inactive thin layer which can be broken when immersed in carbonate, chloride or sulphate solutions. Carbonates, chlorides and sulphates media can be found in concrete when using contaminant aggregates, or adding CaCl₂ (as an accelerator) during the mixing step or they are found under the effect of sea-water or ground-water on concrete and they can also result from attack of concrete by the surrounding environment in coastal regions [8]. Chloride and sulfate are aggressive anions. Chloride ions are being present as original constituents of concrete mixture or as a result of penetration from the environment. Sulfate ions, on the other hand, are found to be actively participated in the corrosion of reinforcing steel especially in the area of the Middle East [9].

In the present investigation, the corrosion behavior of steel reinforcement in cement has been studied with partial replacement of cement by Metakaolin from 5% to 20%.

Experimental Procedure

Materials Used

The materials used in this investigation were Ordinary Portland cement (OPC) produced from National Cement Company and MK produced by controlled thermal treatment of kaolin. A poor Greek kaolin with a low kaolinite content was thermally treated at 650°C for 3 h and the produced Metakaolin (MK) was ground to the appropriate fineness. The chemical analyses of these raw materials are shown in Table 1

Table 1: Chemical Compositions of Raw Materials

Chemical Composition (%)	Na ₂ O	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	Cao	TiO ₂	Fe ₂ O ₃	L.O.I
OPC	0.601	4.227	15.892	0.175	2.539	0.103	67.330	0.510	5.292	-
MK	0.077	28.729	52.002	0.126	0.405	0.136	0.605	4.247	2.348	10.9

Sample Preparations

Cylindrical specimens of 60 mm diameter and 100 mm height were cast with an embedded steel bar of 12 mm in diameter and 100 mm in height were prepared for corrosion test. The steel bars were mechanically polished to remove the firmly adherent mill scales on the surface and cleaned by deionised water, dried with acetone then coated with epoxy leaving 1 cm² uncoated. The chemical compositions of reinforcing steel are shown in Table 2

Table 2: Chemical Composition of Reinforcing Steel

Element	C	Si	Mn	P	S	Cr	Ni	Al	Fe
Wt %	0.323	0.169	0.782	0.0321	0.0186	0.0188	0.0135	0.0333	bal

Different mixes were made by substitution 0, 5, 10, 15, 20 wt. % of cement by MK. The mixes were denoted as M₀, M₁, M₂, M₃ and M₄ as shown in Table 3. The cylindrical specimens were vibrated mechanically to assist compaction. After 24 h of setting the cylindrical specimens were demoulded and subjected to water curing for 7 days in order to avoid any contamination.

Table 3: Mix Composition of the Prepared Cements (Wt %)

Mix No.	OPC	MK	Water
M ₀ (OPC)	100	-	0.24
M ₁ (5 % MK)	95	5	0.24
M ₂ (10 % MK)	90	10	0.24
M ₃ (15 % MK)	85	15	0.24
M ₄ (20 % MK)	80	20	0.24

Corrosion Measurements

Two different electrochemical methods were used to evaluate the corrosion behavior of reinforcing steel bar. The open circuit potential and Tafel Plot polarization measurements were performed using the Voltalab 40 Potentiostat PGZ301 made in Germany.

Open Circuit Potential (OCP)

OCP measurements were often used as an indication of the corrosion risk of the steel. The reinforcing steel embedded in the cement paste was employed as working electrode and a saturated calomel electrode (SCE) as reference electrode. Bi-weekly readings were recorded for potential till 90 days of exposure period. Before each measurement, the potential was recorded until it reached an almost stable value, which was the corrosion potential, E_{corr} .

Tafel Polarization Experiments

Tafel polarization technique was used to determine the corrosion parameters; corrosion potential, corrosion current and corrosion rate of reinforcing steel bars embedded in cement paste. The potential of the steel electrode was scanned at a scan rate of 2 mV/s. The tests were initiated at 250 mV below the corrosion potential (E_{corr}) and terminated at 250 mV above it, while recording the polarization current density (i). The Tafel equation is an empirical relation between the overpotential of the electrode and the current density passing through the electrode:

$$\eta = a + b \log i \quad (1)$$

Where η is the overpotential; i is the current density; a and b are characteristic constants of the electrode system. A plot of electrode potential against the logarithm of the current density is called the "Tafel plot" and the resulting straight line the "Tafel line". "b" is the "Tafel slope" that provides information about the mechanism of the reaction, and "a" the intercept, provides information about the rate constant (and the exchange current density) of the reaction.

The corrosion rate, C.R. (μm consumption of steel per year) can be computed using Faraday's Law as follows

$$C.R. (\mu\text{m}/\text{year}) = 3.3 i_{corr} M/zd \quad (2)$$

Where; z = ionic charge (3 for iron), M = atomic weight of metal (55.85 for iron), d = density of iron, 7.9 g/cm³, and i_{corr} = corrosion current density, μA/cm².

RESULTS AND DISCUSSIONS

Open Circuit Potential (OCP)

Figure 1 & 2 show the potential-time behavior of reinforcing steel bar embedded in cement paste without and with different percentages of MK in 3.5% NaCl and 5% MgSO₄ solutions, respectively. The open circuit potential was monitored periodically for a period of 90 days of exposure. The corrosion potential of reinforcing steel bar in Portland cement was found to be a good indicator of corrosion activity. If the potential between saturated calomel electrode (SCE) and steel bar was more positive than -200 mV, it is considered a non corrosion (passive) state for steel, while values was more negative than -250 mV indicates active corrosion. Between -200 and -250 mV, the steel surface may be active or passive [10].

Samples immersed in 3.5% NaCl solution, Figure 1, attained active potential and the time of active potential does not depend on the increase of the concentration of MK percentage in the specimen except for 20 % MK replacement which shows a noticeable shift of potential towards positive direction at the end of exposure period. Regarding samples immersed in 5% MgSO₄ solution, Figure 2, a steady state potential was observed and remained passive in 5 % MK, while the steady state potential was observed active in the range of 10-20% of MK. The effect of time on the active potential was more pronounced in 15% MK.

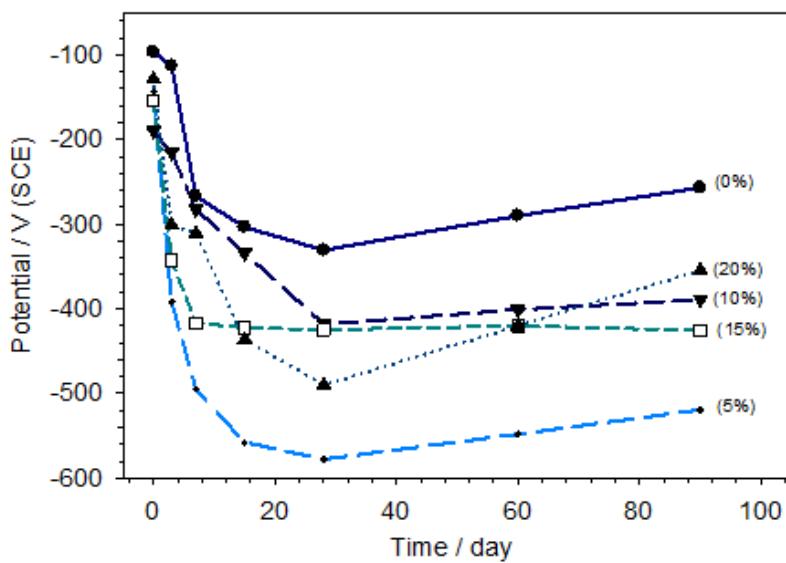


Figure 1: Potential Variation with Time for Reinforcing Steel Impeded in Cement Paste with Different Percentage of Metakaolin Paste in 3.5 % NaCl

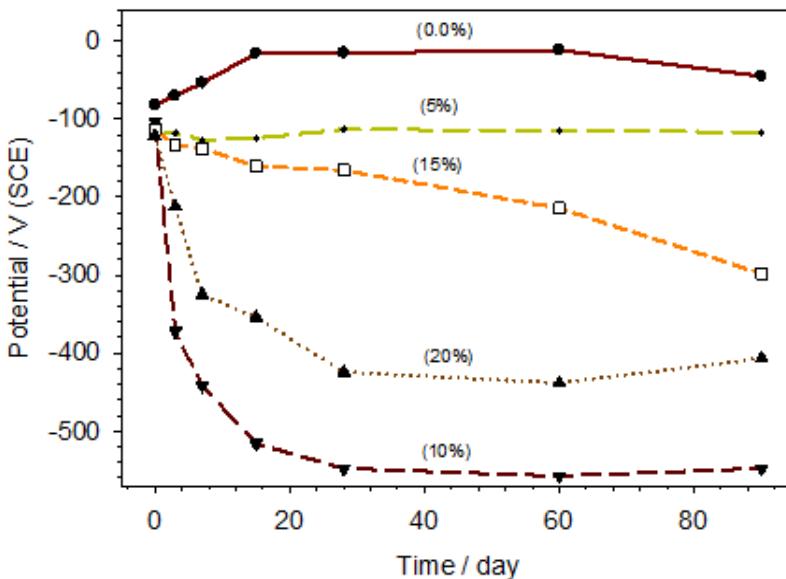


Figure 2: Potential Variation with Time for Reinforcing Steel Impeded in Cement Paste with Different Percentage of Metakaolin Paste in 5 % MgSO₄

Tafel Polarization Experiments

The progress of the corrosion and consequently the performance of the MK admixed concretes was monitored by means of the corrosion current density and the corresponding corrosion rates. Tafel polarization technique had employed at scan 2 mV/s. The linear polarization measurements of reinforcing steel in cement paste with and without MK immersed 90 days in 3.5% sodium chloride solution are presented in Figure 3. The values of corrosion parameters, corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarization resistance (R_p) and corrosion rate (C.R), are recorded in Table 4. It can be seen from Figure 2 and Table 4, that the control system curve (OPC) without addition of MK has lower corrosion potential than concretes with MK.

From Table 4, it is found that there is a nonsystematic decrease in the corrosion current density of the concretes. Also, the corrosion rate values decreased in the presence of 5, 10, and 20 % MK while increased in the presence of 15%

MK. The effect of 3.5% NaCl solution on the control concrete is more pronounced than MK concretes. These results demonstrate that control concrete shows active corrosion behavior, whereas MK concretes generally stayed in moderate corrosion region. For a given chloride concentration, the utilization of MK especially at 20 % provided good performance to the concrete in terms of corrosion resistance. The corrosion enhancement by chloride was attributed to the dissolution of Portland layer followed by de-stabilization of the film bond by migration of chloride ions [12, 13].

Since MK is known for its beneficial contribution on the permeability properties of the concrete [3], one of its main effects in mitigating the harmful effect of chloride ion contamination can be performed by affecting the pore structure of the concrete. Decrease in the average pore size and total porosity of concrete results in reduced capillarity of concrete [3-6, 14, 15].

Table 4: Corrosion Parameters of Reinforcing Steel Impeded in Cement Paste after 90 Days Immersion in 3.5% Sodium Chloride

System	E _{corr} (mV)	I _{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate ($\mu\text{m}/\text{y}$)
OPC (control)	-316.1	2.7924	32.66
5 % MK	-644.5	2.8048	32.80
10 % MK	-510.1	1.6003	18.71
15 % MK	-506.4	3.5679	41.73
20 % MK	-461.6	1.0603	12.40

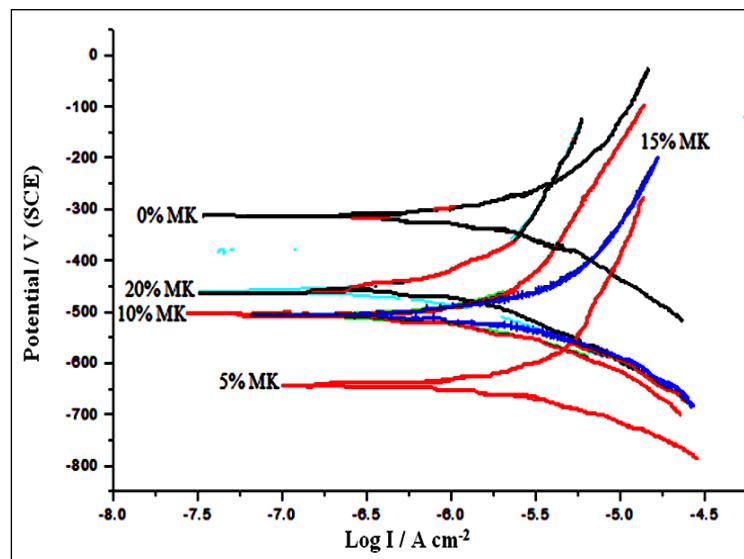


Figure 3: Tafel Polarization Curves for Reinforcing Steel Immersed in 3.5 % NaCl

The Tafel polarization curves of reinforcing steel impeded in cement paste after 90 days immersion in 5% magnesium sulfate is presented in Figure 3. The values of corrosion parameters; corrosion potential (E_{corr}), corrosion current density (I_{corr}), polarization resistance (R_p) and corrosion rate (C.R), were recorded in Table 4.

Table 5 shows that the corrosion potential shifted towards negative values with additions of MK in comparison to the control sample. Corrosion current and corrosion rate for 5% MK addition was found to be less than that of the control sample. The addition of 10 % MK showed higher corrosion current and corrosion rate compared to other concrete systems. In case of 20 % MK addition, corrosion current and corrosion rate was found to be slightly higher than the control

system. Therefore, the addition of 5%, 10% and 15% MK showed less corrosion rates than the control sample. The polarization resistance values show the same trend. Modification of the original film by sulfate ions may lead to the formation of ion sulfate film leading to the reduction of film passivity [10, 16-17].

Tafel polarization measurements of reinforcing steel impeded in cement paste with and without addition of Metakaolin after immersion of 90 days in 3.5% NaCl and 5% MgSO₄ solution showed that 20% Metakaolin replacement of cement showed the best corrosion resistance in 3.5% NaCl solution while the 5% addition of Metakaolin gives the highest corrosion resistance in the 5% MgSO₄ solution.

Table 5: Corrosion Parameters of Reinforcing Steel Impeded in Cement Past after 90 Days Immersion in 5% MgSO₄

System	E _{corr} (mV)	I _{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion Rate ($\mu\text{m}/\text{y}$)
OPC(control)	-171	0.8144	9.525
5 % MK	-246.2	0.3966	4.639
10 % MK	-639.1	0.4567	5.67
15 % MK	-441.9	0.4487	5.248
20 % MK	-509.3	0.9381	10.97

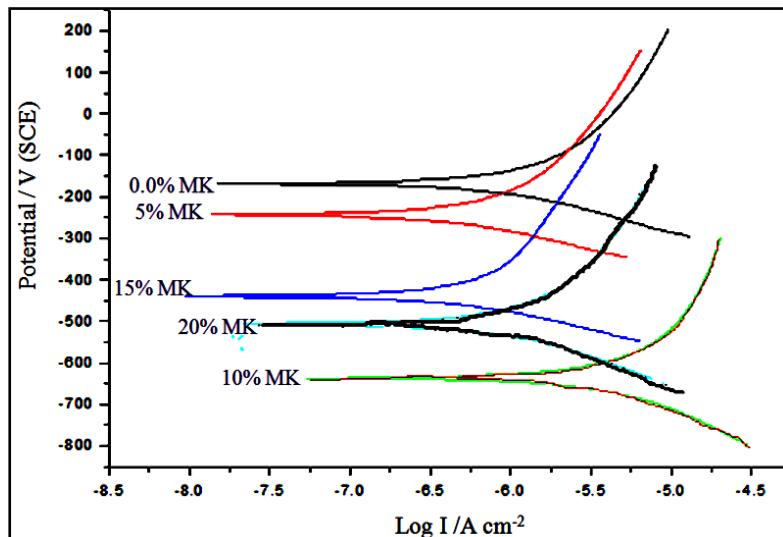


Figure 4: Linear Polarization Curves for Reinforcing Steel Immersed in 5 % MgSO₄ after 90 Days

CONCLUSIONS

- MK plays an important role in reducing the corrosion of steel in cement which exposed to chloride or sulphate media.
- The open circuit potential measurements showed that the sample with 5 % MK immersed in 3.5 % NaCl solution has more negative potential than the control sample while it has less negative potential if immersed in 5 % MgSO₄ solution. Consequently, chloride ions are more aggressive for steel bar in cement than sulfate ions.
- Tafel Plot experiments illustrate that 20% MK replacement of cement gives the highest corrosion resistance concrete in 3.5 % NaCl solution. On the other hand, 5% MK replacement of cement gives the highest corrosion resistance concrete in 5 % MgSO₄ solution.

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